PB83-163402

Phosphorus Inactivation by Zirconium in a Eutrophic Pond

(U.S.) Corvallis Environmental Research Lab., OR

1982

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1. REPORT NO.	2.	3
EPA-600/J-82-223	JOURNAL ARTICLE	PB83-163402

4. TITLE AND SUBTITLE	5. REPORT DATE
Journal Article: Phosphorus inactivation by zirconium in a eutrophic pond	1982
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) William D. Sanville, Charles F. Powers, Gerald S. Schuytema, Francis S. Stay, and William L. Lauer	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Corvallia, Oregon 97333	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Same	13. TYPE OF REPORT AND PERIOD COVERED Journal Article - in house
	14. SPONSORING AGENCY CODE EPA/600/02

15. SUPPLEMENTARY NOTES
Published in Journal Water Pollution Control Federation 54(5):434-443, May 1982

16. ABSTRACT

Eutrophication control remains a critical phase in the management of freshwater ecosystems. A fundamental approach is limitation of nutrients through diversion or advanced waste treatment. However, trophic state improvement may not be obtained in systems with poor flushing characteristics or in systems that recycle large quantities of nutrients from enriched sediments. In such cases in situ treatment is a possible option. The authors conducted a systematic laboratory evaluation of a group of potential phosphorus inactivants. Zirconium tetrachloride, zirconyl chloride, lanthanum (La) rare earth carbonate, lanthanum rare earth chloride, sodium aluminate, aluminum sulfate, sodium tungstate, titanium sulfate, and a crude zirconium refinery waste were evaluated for P-removal efficiency and toxicity to aquatic organisms. The La and Zr compounds were the most efficient P inactivants. However, tests revealed the La compounds to be toxic, and Zr was selected as the inactivant for field testing. The basic objectives of the field study were to determine whether primary production in a natural body of water could be reduced by Zr inactivation of P, and whether there were undesirable biological side effects.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to public	Unclassified	11
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA-600/J-82-223
JOURNAL ARTICLE

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Phosphorus inactivation by zirconium in a eutrophic pond

William D. Sanville, Charles F. Powers, Gerald S. Schuytema, Francis S. Stay, William L. Lauer

Eutrophication control remains a critical phase in the management of freshwater ecosystems. A fundamental approach is limitation of nutrients through diversion or advanced waste treatment. However, trophic state improvement may not be obtained in systems with poor flushing characteristics or in systems that recycle large quantities of nutrients from enriched sediments. In such cases, *in situ* treatment is a possible option.

Nutrient inactivation relies on the addition of a chemical complexing agent to reduce the availability of essential plant nutrients. Recent inactivation studies have emphasized phosphorus (P) removal. Dunst *et al.*[1] summarized a number of such studies in the U. S. and Europe, most of which employed aluminum compounds. Jernelöv[2] reported phosphorus reduction and increased dissolved oxygen in Lake Langsjön, Sweden, using aluminum sulfate; and Peterson *et al.*[3] reported similar changes in Horseshoe Lake, Wis. Aluminum sulfate also was added to West Twin Lake at Kent, Ohio,[4] and at Liberty Lake, Wash., where it was reported to have removed up to 90% of the dissolved phosphorus.[5] Sanville *et al.*[6] noted decreases in phosphorus and chlorophyll *a* levels in a small pond treated with sodium aluminate. Fly ash was used in an inactivation experiment on Lake Charles East, Ind.[7] In laboratory tests Peterson *et al.*,[8] and Kumar and Rai[9] demonstrated the phosphorus-removing effectiveness of zirconium (Zr) salts.

The generally positive results obtained by previous workers, and the need for practical alternative methods for controlling eutrophication in lakes, encouraged the authors to conduct a systematic laboratory evaluation of a group of potential phosphorus inactivants.[8] Zirconium tetrachloride, zirconyl chloride, lanthanum (La) rare earth carbonate, lanthanum rare earth chloride, sodium aluminate, aluminum sulfate, sodium tungstate, titanium sulfate, and a crude zirconium refinery waste were evaluated for P-removal efficiency and toxicity to aquatic organisms. The La and Zr compounds were the most efficient P inactivants. However, tests revealed the La compounds to be toxic, and Zr was selected as the inactivant for field testing.

Reduced phytoplankton was caused by inhibition of phosphorus cycling from the sediments.

The basic objectives of this field study were to determine whether primary production in a natural body of water could be reduced by Zr inactivation of P, and whether there were undesirable biological side effects.

METHODS AND MATERIALS

The study site, Cline's Pond, is located 27 km north of Corvallis, Oreg. (Figure 1). The pond was constructed in 1954, has a 0.4-ha surface area, 9 400-m^3 volume, 4.5-m maximum and 2.4-m mean depth when full. Some slope wash enters from a 1-ha cultivated field, and under conditions of intense rainfall, some could enter from a stand of coniferous trees. Groundwater infiltration is evident. During periods of high water, the pond drains from a surface outlet.

The pond was used for an aeration study in 1969[10] and a nutrient inactivation experiment with sodium aluminate in 1971.[6] In October 1972, it was drained and as much as possible of the surficial sediment removed. The pond refilled naturally the following winter. In September 1973, 16.1 kg of P as a commercial liquid fertilizer was added to increase productivity.

The pond was divided into two sides of approximately equal area and volume with a vinyl curtain on February 27, 1974 (Figure 1). It was sealed to the bottom with sand bags. One side was designated the control, and the other the experimental side to which the Zr would be added. Maximum depth was 3.5 m in the control and 4.5 m in the experimental side. Bottom contour and composition were similar. Sediments consisted of organic silt at the north end of the experimental side, whereas clay was predominant at the south end. The control side sediments ranged from silt and clay in the north to clay in the south.

The pond drained only from the control side during the first 8 months of the study, resulting in water move-

Journal WPCF, Volume 54, Number 5
pp. 434-443, May 1982

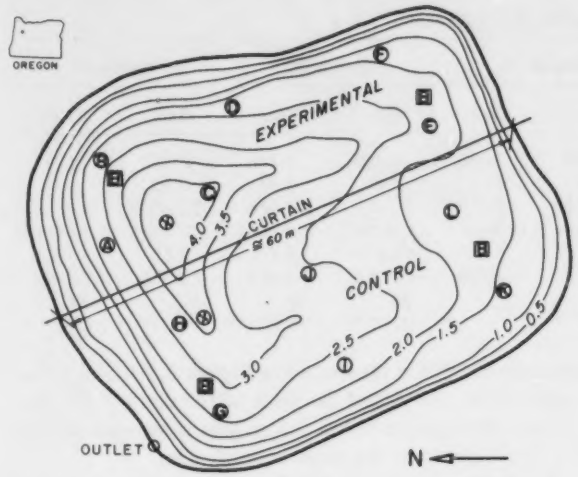

Figure 1—Bathymetric map of Cline's Pond showing sampling sites for water (⊗), Benthos (▣), and sediment cores (Ⓐ - Ⓛ).

ment from the experimental to the control side. A standpipe was installed in the experimental side in November 1974 to carry overflow directly to the pond outlet.

Transparency was measured with a black and white 20-cm Secchi disk, and turbidity with a nephelometer. Analyses of major nutrients and metals were in accordance with EPA procedures.[11] Zirconium analysis was by inductively coupled plasma optical emission spectrometry. Chlorophyll *a* was determined by a modification of Strickland and Parsons[12] that included phaeophytin correction.

Phytoplankton were counted and identified using an inverted microscope.[13,14] Numbers were expressed as cells/ml except for certain colonial forms that were counted as individuals. The filamentous forms, such as *Melosira* and *Oscillatoria*, were given 1 count per 100 μm of filament. Benthos were collected with a 15 × 15-cm Ekman grab and washed in a 0.59-mm mesh screen. Adenosine triphosphate (ATP) was extracted with boiling Tris buffer and analyzed with an ATP photometer.[15,16] Carbon-14 primary productivity methodology was similar to that of Vollenweider.[17] Algal assays were in accordance with the Algal Assay Procedure, Bottle Test.[18]

The pond was sampled intermittently after October 1972. Following installation of the curtain, sampling was weekly until the Zr addition. After Zr treatment, the frequency was every 2 days for the first week, weekly through the fall of 1974, monthly during the following winter and spring, and weekly or every 2 weeks during the rest of 1975.

Analysis of data from three sites of each side of the curtain demonstrated that sampling the deep station on each side was sufficient for limnological characterization. Water samples were taken at the surface and at l-m intervals using a Van Dorn sampler.

Triplicate macrobenthos samples were collected monthly from near the north and south ends of each side (Figure 1), and vertical tows for zooplankton were taken at the same time in the middle of each side with a 0.34-mm mesh net. Two hundred-fifty 4- to 7-cm Kamloops trout (*Salmo gairdneri* Richardson) were stocked in each side 1 week prior to the Zr addition. Fish samples were frozen and retained for background Zr analysis. Adults were collected in June and October 1975. Macrophytes, tadpoles, littoral insects, and sediment were also collected in October 1975 for Zr analysis. Individual samples were freeze-dried, homogenized, and analyzed separately. Sediment cores were taken from each side and sectioned according to visibly different sediment types.

Total chemical and biological quantities were obtained for each side by multiplying the concentration at a given depth by the volume of the water stratum that it represented and summing the products. The surface concentration was multiplied by the volume of the 0- to 0.5-m stratum, the l-m concentration by the volume of the 0.5- to 1.5-m stratum, and so on. Average concentrations were obtained by dividing the total quantity by the total volume of that side of the pond.

The experimental side was treated on March 26–27, 1974, with 63 kg of anhydrous zirconium tetrachloride mixed with water. The quantity was based on laboratory jar tests of Cline's Pond water collected 2 days prior to treatment. The calculated final concentration of Zr in the experimental side was approximately 5 mg/l. Distribution into the pond was through a manifold system from an outboard powered boat. A second manifold was used for addition of sodium hydroxide (NaOH) to counteract lowering of pH. Both sides were mixed by making rapid boat traverses.

RESULTS

Upon addition of the Zr, a white floc that tended to settle rapidly developed. Soon many dead cladocera were seen and approximately 20 trout were observed at the surface, behaving as if under stress, though no dead fish were noted. Brownish green surface streamers formed, apparently the product of lysing *Volvox aureus* (Ehrenberg), which was very abundant that day.

Initially, NaOH was added to counter an anticipated pH decrease caused by the zirconium tetrachloride. However, surface pH was near 10, and although values behind the Zr manifold dropped to 7.5, there was a natural recovery to 8.5 to 9.0. NaOH addition was discontinued.

Zirconium addition was completed on March 27. NaOH addition was resumed because pH in the experimental side had fallen to 7.0 to 8.0 compared to

Table 1—Characteristics of the experimental and control sides prior to inactivation.

	February 27		March 6		March 13		March 20		March 25	
	Exp.	Cont.	Exp.	Cont.	Exp.	Cont.	Exp.	Cont.	Exp.	Cont.
TP, mg/l	0.197	0.213	0.187	0.188	0.260	0.256	0.165	0.178	0.121	0.131
TIN, mg/l	1.40	1.39	1.36	1.35	1.26	1.29	1.06	1.08	0.96	1.14
Temp., °C	6.6–6.8	6.5	6.5–6.7	6.5–6.8	7.2–7.5	7.3–7.8	7.5–9.4	7.7–9.6	8.2–12.0	8.2–12.0
DO, mg/l	12.2–14.1	12.1–12.5	12.3–12.5	12.9–13.5	12.7–13.4	12.8–13.1	7.8–13.0	8.2–12.2	4.7–15.8	4.5–14.5
Secchi disk, m	0.8	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
pH	—	—	6.9–7.1	7.1–7.3	7.2–7.4	7.4–7.5	6.9–8.5	7.1–9.3	7.2–9.8	7.2–9.8
Turbidity, NTU	—	—	33	34	33	33	29	26	20	24

control values of 9.5 to 10.0. A total of approximately 13 kg of NaOH was added over the 2 days. No dead or distressed organisms were observed the second day.

Before inactivation, limnological characteristics showed both sides were similar (Table 1). Conditions 1 day before treatment, 1 day after treatment, and 1 week after treatment are summarized in Table 2. Both sides were stratified with respect to temperature and dissolved oxygen the day before treatment; this stratification had weakened by the end of treatment. Transparency and turbidity did not change measurably. Maximum pH decreased in both sides. Total phosphorus, which had reached a maximum of approximately 2.30 mg/l after fertilization, had been declining in both sides at the time of Zr addition (Figure 2). By April 3 the control side had begun to level off, whereas the experimental side continued a rapid decline. Total inorganic nitrogen seemed unaffected by the treatment.

Algal assays of water collected in May 1974 demonstrated the control side to be more productive. The tests indicated that P, not N, was the limiting nutrient in the experimental side at that time.[19]

Table 3 summarizes the long-term effectiveness of the inactivation. During the first year, total phosphorus (TP) and all measures of biomass generally were lower in the experimental side than in the control. Transparency was considerably better in the experimental side also. The control side improved the second year. After January 1975, for instance, TP was generally lower in the control side.

A dramatic increase of TP on both sides during the summer of 1974 is illustrated in Figure 2. Although the upper 1.5 m accounted for most of the control side increase, the stratum below 3.5 m was most responsible for the increase in the experimental side.

Total inorganic nitrogen decreased rapidly in both sides until mid-June, when it stabilized at very low levels (Figure 3). Low levels were established again during the summer of 1975 after substantial winter increases.

Figure 4 is a photograph of the pond taken on August 16, 1974. The transparency was 3.5 and 0.5 m on the experimental (lower) and control sides, respectively. Although control transparency improved the second year, the average was still less than in the experimental side (Table 3).

Chlorophyll *a* (Figure 5) and primary productivity (Figure 6) had patterns similar to TP (Figure 2). Statistically, however, the correlations were poor. Likewise, ATP did not correlate with other parameters.

Soon after inactivation, phytoplankton increased in both sides; by mid-May, there were consistently greater numbers in the control (Figure 7a). By the end of July, the control contained over 200 000 cells/ml; in contrast, the experimental side peaked at about 30 000. Both sides decreased to winter minima in December. In 1975 phytoplankton was much reduced in the control, with peak numbers reaching about one-fourth those observed in 1974. In the experimental side, numbers remained about the same.

Anabaena circinalis Rabenhorst was the predominant alga during the summer of 1974, especially in the control, where it constituted essentially the entire July

Table 2—Limnological conditions 1 day before, 1 day after, and 1 week after inactivation.

	March 25		March 28		April 3	
	Exp.	Cont.	Exp.	Cont.	Exp.	Cont.
TP, mg/l	0.121	0.131	0.071	0.134	0.058	0.104
TIN, mg/l	0.96	1.14	0.95	0.92	0.87	0.87
Temp., °C	8.2–12.0	8.2–12.0	9.8–10.4	8.3–10.2	10.5	10.2–10.7
DO, mg/l	4.7–15.8	4.5–14.5	7.3–10.5	3.1–9.8	9.1–9.5	8.5–8.9
Secchi disk, m	0.7	0.7	0.7	0.8	0.9	1.0
pH	7.2–9.8	7.2–9.8	6.6–6.9	6.2–7.8	6.7–6.8	6.9
Turbidity, NTU	20	24	24	23	16	23

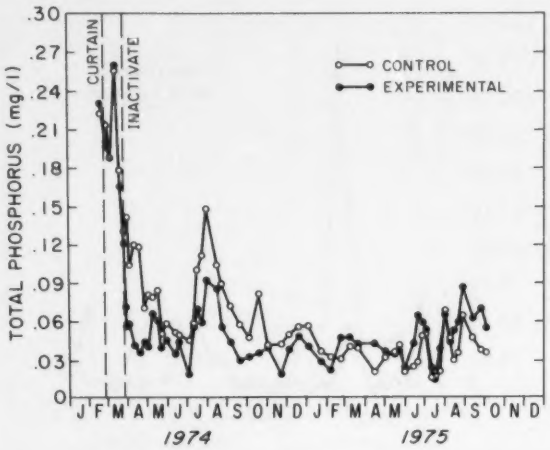

Figure 2—Comparison of total phosphorus (TP) concentrations in the Experimental and Control sections.

peak biomass (Figure 7b). In the experimental side it accounted for only slightly more than one half the total during the July peak. The principal winter algae on both sides were flagellated Chrysophyta. The 1975 growth pattern of *A. circinalis* differed from that of 1974. Maximum numbers occurred in the experimental side in August, whereas the control peaked in July.

Emergent macrophytes were about equally distributed along the shoreline of both sides throughout the experiment. Submerged forms were much more abundant in the experimental side, where they were often visible over approximately one-third of the bottom. In July 1975, *Potamogeton* sp. covered a surface area of about 45 m^2 near the south end of the experimental side. No such growths were seen in the control.

Floating mats of *Spirogyra* were frequently observed only in the control side during the summer of 1975, covering at their maximum approximately 25 percent of the control surface in early May.

Benthic macroinvertebrates collected 5 days after inactivation revealed no dead or apparently distressed organisms. The predominant benthic macroinvertebrates throughout the experiment, in both sides, were Chironomidae, Chaboridae, and Oligochaeta (Figure 8). Increasing numbers and variety characterized the benthic population. Trichoptera, Hydracarina, Anisoptera, Coelenterata, and Turbellaria appeared for the first time after the Zr addition, the latter three on the experimental side only. The greatest total numbers appeared in September 1975, when *Chaoborus* sp. aver-

Table 3—Long-term effects of inactivation.

Side	Parameter	Max.	Min.	Avg. (n, SE)	Inclusive dates
			1974		
Exp.	TP (mg/l)	0.09	0.02	0.05 (21, 0.00)	4/3–10/3
Cont.	TP	0.15	0.05	0.08 (21, 0.01)	"
Exp.	TIN (mg/l)	0.934	0.014	0.282 (21, 0.070)	4/3–10/3
Cont.	TIN	1.064	0.014	0.326 (21, 0.077)	"
Exp.	Secchi (m)	4.3	0.8	2.3 (22, 0.2)	4/3–10/3
Cont.	Secchi	2.5	0.2	1.0 (23, 0.1)	"
Exp.	Chl *a* (mg/m^3)	47.4	0.6	18.2 (19, 3.1)	4/10–10/3
Cont.	Chl *a*	235.6	1.9	60.6 (19, 13.6)	"
Exp.	PP (mg C/m^3/h)	183	17	62 (6, 25)	7/3–10/3
Cont.	PP	958	30	291 (7, 119)	"
Exp.	ATP (µg/l)	1.81	0.02	0.60 (16, 0.13)	4/3–10/3
Cont.	ATP	3.46	0.21	1.29 (17, 0.23)	"
			1975		
Exp.	TP (mg/l)	0.09	0.01	0.05 (20, 0.00)	4/14–10/2
Cont.	TP	0.07	0.02	0.04 (20, 0.00)	"
Exp.	TIN (mg/l)	0.132	0.010	0.026 (18, 0.007)	4/14–10/2
Cont.	TIN	0.953	0.010	0.140 (18, 0.063)	"
Exp.	Secchi (m)	4.0	0.9	2.3 (24, 0.2)	4/4–10/2
Cont.	Secchi	3.0	1.0	1.8 (24, 0.1)	"
Exp.	Chl *a* (mg/m^3)	60.1	5.5	25.9 (13, 4.9)	4/14–10/2
Cont.	Chl *a*	20.5	3.0	12.5 (13, 1.4)	"
Exp.	PP (mg C/m^3/h)	118	7	33 (19, 7)	4/4–10/2
Cont.	PP	65	3	23 (19, 4)	"
Exp.	ATP (µg/l)	2.61	0.09	1.04 (19, 0.15)	4/4–10/2
Cont.	ATP	1.68	0.12	0.83 (19, 0.09)	"

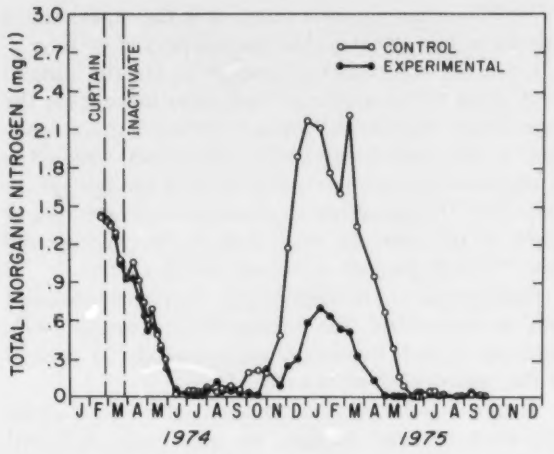

Figure 3—Comparison of total inorganic nitrogen (TIN) concentrations in the Experimental and Control sections.

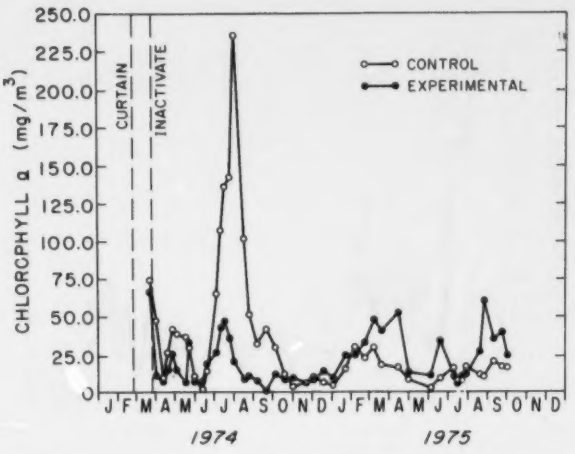

Figure 5—Comparison of Chlorophyll *a* concentrations in the Experimental and Control sections.

aged >32 000/m² at the north control site and >37 000/m² at the north experimental site.

Diversity and areal richness were computed from pooled data and were based mostly on family level identifications (Table 4). Mean "species" areal richness increased significantly (Student's t-test, 0.05 level) in both sides after inactivation but was higher in the experimental side than in the control. There were no significant differences (t-test, 0.05 level) in mean diversity between the two sides prior to or after inactivation, as indicated by H'.[20]

Water samples taken in 1971 and 1972, and again on March 20, 1974, prior to treatment, consistently yielded total Zr concentrations less than 0.005 mg/l (Table 5). Soluble Zr measured approximately 1.9 mg/l in the experimental side on March 28, the day after inactivation, but by April 25, it had dropped twelve-fold. The control increased from 0.021 to 0.120 mg/l over the same period. Total Zr acted similarly. By September 19, both total and soluble Zr in both sides were near or below 0.005 mg/l.

In November 1975, sediment cores were taken for Zr analysis (Figure 1). Concentrations in naturally occurring layers were highly variable (Table 6). The average for experimental side cores was over twice that of the control side, however, and cores from reference areas had only about one-third the Zr concentration of the control side.

There was considerable variability in the Zr content

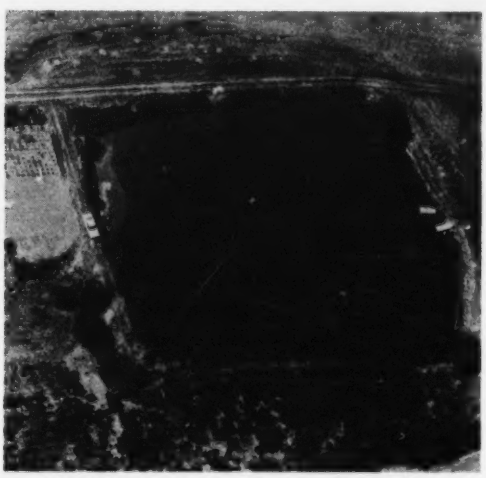

Figure 4—Photograph of Cline's Pond on August 16, 1974, showing the difference in water clarity between the Control (above) and Experimental sections.

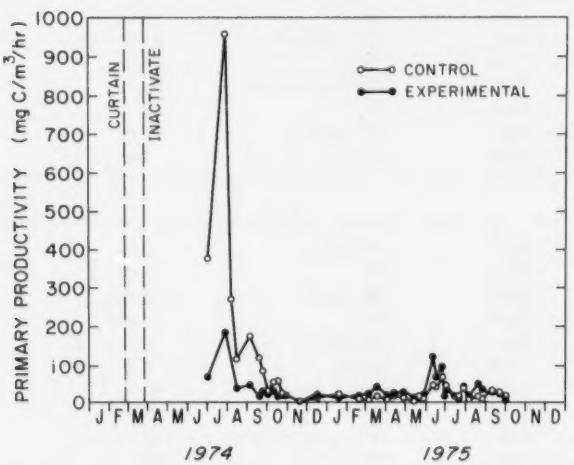

Figure 6—Comparison of primary productivity rates in the Experimental and Control sections.

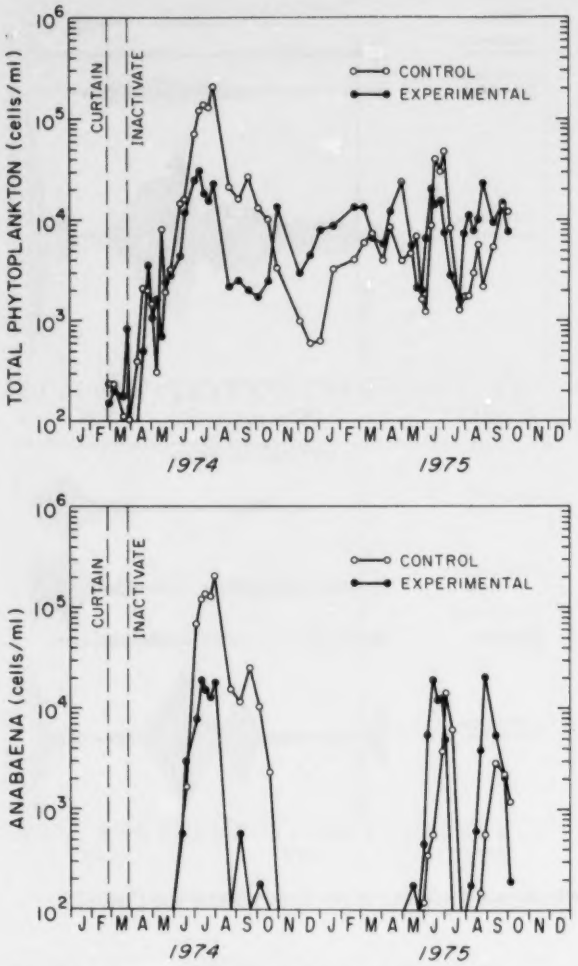
TOTAL PHYTOPLANKTON (cells/ml)
CURTAIN
INACTIVATE
CONTROL
EXPERIMENTAL
J F M A M J J A S O N D J F M A M J J A S O N D
1974
1975
ANABAENA (cells/ml)
CURTAIN
INACTIVATE
CONTROL
EXPERIMENTAL
J F M A M J J A S O N D J F M A M J J A S O N D
1974
1975

Figure 7—Total phytoplankton (7a) and anabaena (7b), comparing Experimental and Control sections.

of pond biota (Table 7). Immediately after treatment, zooplankton in the experimental side showed a dramatic increase. This zooplankton increase was reduced by about 90% by June, and generally decreased through the remainder of the study. A large increase in Zr appeared in control side zooplankton as well, although not until June. A general decrease followed, similar to that of the experimental side.

Trout fingerlings obtained prior to treatment and adults collected in June 1975 both contained <1 μg Zr/g. The Zr content of organisms collected in November 1975 was generally low but extremely variable (Table 7).

DISCUSSION

Immediately following Zr addition, TP declined more rapidly in the experimental than in the control side, probably because of the direct precipitation of dissolved P and P-associated particulate matter. Although external P loading probably occurred during April and May as a result of precipitation and runoff, the summer TP increases observed in both sides were most likely the result of internal loading from the bottom sediments. The pond has no tributaries, and no significant precipitation occurred after May. Any external loading not accounted for (such as dryfall or groundwater infiltration) would have been expected to affect both sides equally. Lower TP in the experimental side probably resulted from immobilization by the Zr. Although internal loading was not eliminated, it was reduced to only one-half that in the control. This reduction was accomplished in spite of an extensive area of organic silt and consequent lowered dissolved oxygen in the experimental side. Near-bottom oxygen values averaged 3.1 mg/l (n = 5, SE = 1.5) in the control during July, and 0.1 (n = 5, SE = 0.4) in the experimental side. The potential for sediment P release, therefore, was greater in the experimental side. It is probable that even less internal P loading would have occurred had more inactivant been added to seal the sediments, as was done by Cooke and Kennedy.[5]

In 1975, control TP did not attain the high levels of 1974. Zirconium concentrations in the water immediately after inactivation, and in the sediment in November 1975, indicated Zr movement past the curtain to the control side. The lowered productivity and TP levels the second year suggest that Zr migration into the control was sufficient to inhibit sediment-water P exchange.

It might be argued that the reduction in productivity and P was a result of attainment of a natural TP steady state, rather than inhibition of P release by Zr. Phosphorus was in a non-steady state when the experiment began, having declined rapidly through the previous fall and winter, suggesting movement toward a new sediment-water TP equilibrium following fertilization. In the summer of 1974, however, maximum phytoplankton biomass and productivity were much greater in the control; in 1975, summer maxima in both sides approximated 1973 values prior to fertilization. If Zr had no effect on P availability, algal productivity in the two sides would have been similar in 1974 and would have decreased at approximately the same rate from 1974 to 1975. The high 1974 control productivity and the low productivity in the experimental side, together with the rapidity with which productivity declined in the control the second summer, strongly suggest mechanisms other than natural equilibrium phenomena. The experimental-control design seems to have performed well during the summer of 1974, but to have been disrupted by winter runoff and gradual leakage under the curtain by the summer of 1975.

There was no evidence that Zr affected the availability of inorganic N. Total inorganic nitrogen (TIN)

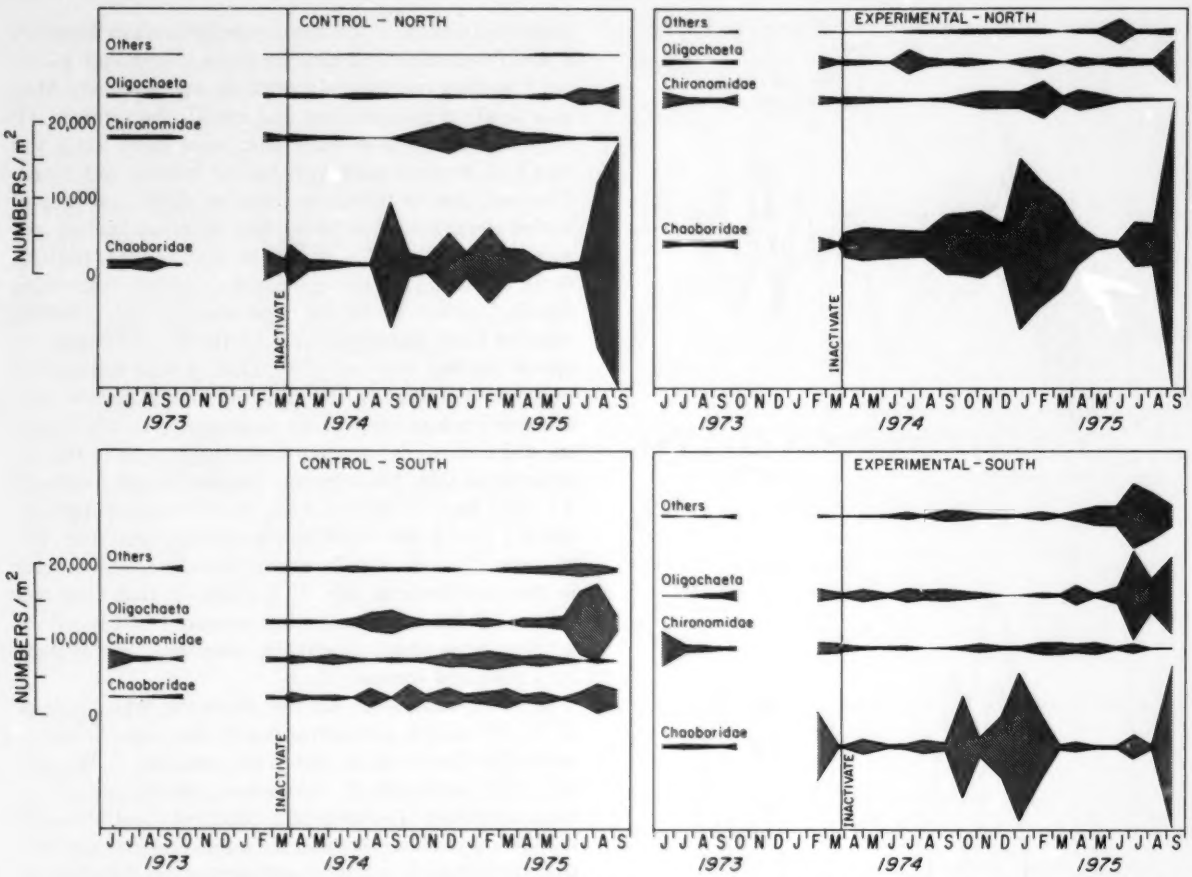

Figure 8—Benthic macroinvertebrate populations at the north and south stations of the Experimental and Control sections.

fell to very low, probably limiting, levels in both sides by mid-June 1974, shortly before the beginning of the summer TP increase. This condition probably favored the N-fixing *A. circinalis*. The substantially higher winter N levels in the control side probably resulted from the much higher productivity in the control the previous summer. The differences in winter TIN do not seem to have had any marked effect on productivity during the following summer.

The primary productivity data have made it clear that observed differences in standing crop between the two sides were not the result of differences in grazing or sedimentation.[21] The algal assay data of May 1974 dismissed acute Zr toxicity as a factor in the reduced productivity.

The absence of acute toxicity or the elimination of taxa, and the general similarity of population growth and composition between the two sides, strongly imply that long-term toxic effects on benthic macroinvertebrates were minimal. Because the "species" richness and diversity computations were based on family or broader-level identifications, the resultant values may only serve as rough indicators of change in community structure. They do not seem to indicate, however, any drastic changes. Observed variations were more likely

Table 4—Mean benthic macroinvertebrate "species" areal richness and diversity.

Index	Experimental	Control
Species areal richness		
No. species/3 grabs		
Pre-inactivation[a] (6/14/73–3/22/74)	5.4	5.4
Post-inactivation[b] (4/01/74–9/10/75)	7.7	6.5
H' $-\sum_{i=1}^{s}\left[\frac{ni}{n}\log_{10}\left(\frac{ni}{n}\right)\right]$		
Pre-inactivation[a] (6/14/73–3/22/74)	0.376	0.378
Post-inactivation[b] (4/01/74–9/10/75)	0.391	0.406

[a] n = 14 triplicate samples each site.
[b] n = 36 triplicate samples each site.

Table 5—Zirconium concentrations (mg/l) of pond water.

Date	Soluble Zr		Total Zr	
	Experimental	Control	Experimental	Control
11/03/71*	—	—	<0.005	<0.005
10/18/72*	—	—	<0.005	<0.005
03/20/74	—	—	<0.005	<0.005
03/25/74	<0.005	<0.005	—	—
03/26-27/74	- - - - - - - - - (Addition of Zirconium) - - - - - - - - -			
03/28/74	≥1.90	0.021	—	—
04/10/74	0.176	0.139	1.226	0.162
04/25/74	0.165	0.120	0.592	0.195
09/19/74	<0.005	<0.005	<0.005	<0.005
10/03/74	<0.005	<0.005	0.007	<0.005
10/31/74	<0.005	<0.005	0.010	0.008
12/08/74	<0.005	<0.005	0.009	0.008
12/18/74	<0.005	<0.005	0.008	0.008

*Pond not divided.

natural expressions of emergence, repopulation, and bottom type. Increases from year to year were probably the result of a continuing repopulation after the 1972 dredging.

Reasons for the variability in Zr content of the biota are not clear. The presence of Zr on the outer surfaces of plankton, benthos, macrophytes, and miscellaneous littoral fauna is a possibility. Additionally, benthic and planktonic organisms may have ingested settled floc. The gut contents of such small animals could represent a large proportion of their total biomass, seemingly indicating high levels of Zr accumulation. The Zr concentrations in trout, on a whole body basis, were the same before and after treatment. The gut contents of fish, however, would be a relatively minor portion of their total body mass. Gut contents were not analyzed separately.

Some monitoring was continued in 1976–77, but on an infrequent, nonroutine basis. No massive algal blooms were observed, and algal productivity seemed much reduced. Vascular aquatic plants seemed to be much more important in the ecology of the pond than before. They were found at nearly all depths in both sides, with both submergent and emergent forms common. The trend toward increased presence of vascular plants may be related to increased water transparency resulting from reduced algal productivity. Rooted plants obtain nutrients from the sediments,[22-24] and would not necessarily be affected by nutrient inactivation in the water or inhibition of internal loading. They might even benefit from precipitation of nutrients to the sediments.

Information relating to the adverse health effects of Zr in aerosol deodorants appeared after this experiment was well under way.[24] The possible relation of such effects to the work reported here is not known.

SUMMARY AND CONCLUSIONS

An experiment was conducted in a eutrophic farm pond to test the efficacy of Zr in reducing the avail-

Table 6—Zirconium content of cores from pond and adjacent reference sites, Nov. 20, 1975.

Experimental			Control			Adjacent reference areas		
Location	Sediment depth (mm)	μg Zr/g	Location	Sediment depth (mm)	μg Zr/g	Location	Sediment depth (mm)	μg Zr/g
A	0–10	148	G	0–10	139		Nearby Pond	
A	10–35	523	G	10–25	133	M	0–40	59
B	0–8	232	H	0–10	297		Field	
B	8–33	841	H	10–35	213	N	0–25	59
C	0–10	788	I	0–5	235	P	0–25	70
C	10–55	878	I	5–25	208			
C	60–65	282				Q	0–150	70
			J	0–10	140			
D	0–10	982	J	10–25	180	R	0–150	67
E	0–2	268	K	0–5	218			
E	2–25	137						
			L	0–10	134			
F	0–5	405	L	10–25	229			
F	5–25	132						
	Mean	468 (n = 12, SE = 93)		Mean	193 (n = 11, SE = 16)		Mean	65 (n = 5, SE = 2)

Table 7—Zirconium concentration (μg/g) of pond biota.

Biota	Date	Experimental	Control
Zooplankton	03/22/74	10	11
	04/01/74	1780	8
	06/11/74[a]	190	550
	08/07/74[a]	80	30
	03/12/75[a]	10	60
	06/11/75	44	30
	08/07/75	13	—
	09/10/75	17	6
Trout, fingerlings	03/20/74	<1	<1
Trout, adults	06/01/75	<1	<1
Tadpoles[b]	11/06/75	≧200	39
		20	56
Benthic invertebrates[b]	11/06/75	8	22
		≧200	31
Miscellaneous littoral fauna from weed beds[b]	11/06/75	20	56
		20	26
Emergent macrophytes[b]	11/20/75	9	4
		—	40
Submergent macrophytes	11/20/75	47	4

[a] Analyst estimated confidence limits up to ±100% owing to small sample size.

[b] Multiple values are single analyses of replicate samples.

ability of P to phytoplankton. The pond was divided into experimental and control sides, and a zirconium tetrachloride solution was added to the experimental side to obtain an approximate final concentration of 5 mg Zr/l. Although some leakage to the control side was observed, dramatic differences in phytoplankton production between the two sides occurred during the first summer. An intensive bloom of *Anabaena circinalis* developed in the control, along with elevated TP.

The reduced phytoplankton production in the experimental side seemed to be caused by inhibition of P recycling from the sediments. Although Zr leakage did not affect results significantly the first summer, an absence of pronounced differences the second year could have been caused by Zr accumulation in the control.

Data on possible biological uptake of Zr by plants and invertebrates are highly variable. No evidence of bioaccumulation in fish was found, and no acute or long-term effects were found in either plants or animals.

ACKNOWLEDGMENTS

Credits. The authors wish to thank the Lester Cline family for use of their facilities and for their unfailing support and cooperation, and Spencer Peterson for his contributions during the planning and inactivation stages of this study.

Authors. At the time this study was conducted, W. D. Sanville, C. F. Powers, G. S. Schuytema, F. S. Stay, and W. L. Lauer were aquatic biologists with the Corvallis Environmental Research Laboratory, U.S. Environmental Protection Agency, Corvallis, Oreg.

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